STUDIES OF SOME COÖRDINATION COMPOUNDS OF PLATINUM, CHROMIUM, AND COBALT

I. OLEFIN COMPOUNDS OF PLATINUM

II. AMINO ACID COMPOUNDS OF CHROMIUM AND COBALT

BY

RAYMOND NEVOY KELLER

A.B., Indiana University, 1937

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1940

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I. OLEFIN COMPOUNDS OF PLATINUM

While compounds in which an olefinic molecule is bonded to a metal differ in no marked way chemically from other types of complex salts, the mechanism of complex formation is obscure in that the coördinated group possesses no lone pair of electrons with which to form the coördinate link.

It has been suggested[1,2] that in the formation of platinum-olefin compounds one of the electron pairs between the doubly bonded carbon atoms of the olefinic molecule shifts so as to form an octet of electrons on one carbon but leaving only a sextet of electrons on the other. The pair of electrons needed by the latter carbon atom, however, is supplied by the platinum which functions as a "donor atom" in this case. The usual electron-pair coördinate bond results and the olefinic molecule occupies only one position in the coördination sphere.

On the basis of such a mechanism, a compound of the type $K[PtCl_3.Un]$ should possess an optically active anion when Un represents a properly substituted olefin. However, attempts to resolve the anion $[PtCl_3.styrene]^-$ with both optically active bases and finely powdered active quartz have been unsuccessful.

Optical activity has been reported[1] for the compounds $[PtCl_2.styrene]_2$ and $[PtCl_2.stilbene]_2$. This optical activity may arise because of the presence of one or more asymmetric carbon atoms due either to a cyclic structure or due to the attachment of the olefin to platinum in accordance with the mechanism outlined above. Attempts to confirm such optical activity by the use of finely powdered *levo-* or *dextro*-quartz were completely unsuccessful.

The method of effecting partial resolution of a racemic solution by preferential adsorption on finely divided optically active quartz was first reported by Tsuchida, Kobayashi, and Nakamura,[3] and used later apparently with some success by Karagunis and Coumoulos,[4] and Stiegman.[1] The effectiveness of this method was investigated in some detail in the present study. Tsuchida, Kobayashi, and Nakamura reported an observed rotation of $+0.06°$ (sodium D line) in their partial resolution of the compound

$[Coen_3]Br_3.3H_2O$ by this method. Using this compound and quartz powder derived from large individual crystals of *levo-* or *dextro*-quartz, and employing a variety of conditions, no indication of asymmetric adsorption was obtained in this investigation. These results raise some question as to the general usefulness of this method.

A comprehensive survey was made of the literature pertaining to metal-olefin compounds. Olefin compounds have been reported not only for platinum but also for palladium, iron, zinc, iridium, aluminum, copper, silver, and mercury. All of these complexes are apparently of the same general type; consequently the metal-olefin bonds in these compounds are perhaps also similar. The various structures which have been proposed for these complexes were criticized.

II. AMINO ACID COMPOUNDS OF CHROMIUM AND COBALT

The *a*-amino acids have been reported[5,6,7] to form cobalt and chromium complexes, most of which are characterized by high stability and low solubility. In these complexes the amino acid molecule usually functions as a bidentate group in which the hydrogen of the carboxyl group has been replaced and the nitrogen of the amino group is coördinately bound to the metal. These complexes, however, have received only scant investigation. It was felt that by initiating a systematic study of these compounds some correlation between the structure of an amino acid and its coördinating ability might be revealed. The general insolubility of these compounds also suggests the possibility of obtaining specific precipitating reagents for some of the amino acids.

In preparing these complexes by a variety of methods, it was discovered in this study that pure amino acid complex compounds are usually not obtained because of hydrolysis. Elucidation of this hydrolysis reaction indicates that successively more complex products are formed as the reactants are heated together. The degree of complexity depends upon the amino acid, the original chromium or cobalt compound used, the basicity of the solution and the duration of the heating period. The first type of insoluble complex which forms appears to be a non-ionic mononuclear structure in which three amino acid molecules are coördinated about the metal. However, on continued heating one of the amino

acid molecules apparently splits off and a doubling up occurs to give a dinuclear type in which the two metal atoms are bridged by two OH groups. The dinuclear type can in turn hydrolyze to yield perhaps a trinuclear complex, and indications are that hydrolysis does not stop even there.

From the results obtained in this study, it appears that substitution beyond the amino group influences the coördinating tendency of an α-amino acid and is associated in some manner with the character of the complex produced. The α-amino acids studied can be divided roughly into two groups—those which usually form soluble complexes and those which form insoluble complexes. The first group includes the following acids: alanine, allothreonine, arginine, aspartic acid, glutamic acid, glycine, histidine, lysine, and serine. The following fall in the second group: α-amino butyric acid, isoleucine, leucine, methionine, phenylalanine, phenylglycine, tryptophane, valine, and possibly cystine. In general, an alkyl or aromatic group on the β-carbon atom favors the formation of insoluble complexes, whereas the presence of an hydroxyl group in the same position favors the formation of soluble compounds. In those cases investigated, functional groups in the carbon chain seem to contribute toward soluble complex formation.

The insoluble amino acid complexes of chromium and cobalt are very inert substances. They possess no sharp melting points but darken gradually when heated. At higher temperatures charring and ignition occur. These substances as a class are lavender or purple in color. Some, however, are of a distinctly red shade. In general, the cobalt complexes are more highly colored, show a greater color variety, and are more stable than the corresponding chromium compounds. The latter is not surprising in view of the relative stabilities of other cobalt and chromium coördination compounds.

The separation of the amino acids through complex formation does not appear promising. The difference in the tendencies of the amino acids to coördinate is not sharply defined, the amino acids are incompletely precipitated even in the presence of an excess of a complex salt, and the precipitates in most cases are not of definite composition due to hydrolysis.

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VITA

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